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# Thermally driven defect formation and blocking layers at metal-ZnO interfaces

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The authors used depth-resolved cathodoluminescence spectroscopy and current-voltage measurements to probe the temperature-dependent formation of native point defects and reaction layers at metal-ZnO interfaces and their effect on transport properties. These results identify characteristic defect emissions corresponding to metal-Zn alloy versus oxide formation. Au alloys with Zn above its eutectic temperature, while Ta forms oxide blocking layers that reduce current by orders of magnitude at intermediate temperatures. Defects generated at higher temperatures and/or with higher initial defect densities for all interfaces produce Ohmic contacts. These reactions and defect formation with annealing reveal a thermodynamic control of blocking versus Ohmic contacts. © 2007 American Institute of Physics. [DOI: 10.1063/1.2772664]

ZnO is a promising material for next-generation opto- and microelectronics.<sup>1,2</sup> However, several technological hurdles remain before devices are realized, including the fabrication of thermally stable rectifying and Ohmic contacts. Previously, the authors showed how oxygen plasma processing removes adsorbates, subsurface hydrogen, and deep levels to improve Schottky barriers.<sup>3,4</sup> In this letter, we emphasize the importance of thermally induced interface chemical interactions in forming blocking layers and defects. These interactions depend on the metal-ZnO bonding, the annealing temperature, and the initial bulk native defect concentration. Depth-resolved cathodoluminescence spectroscopy (DRCLS) measurements reveal two classes of metal-ZnO reactions that determine the contacts' current-voltage (*I-V*) properties and thermal stability. DRCLS emissions at 2.1 vs 2.5 eV appear characteristic of Zn- versus O-deficient native point defects based on alloy versus oxide formation, respectively. High work function metals such as Au, Pt, and Pd form high Schottky barriers that degrade with thermally induced alloying. Oxide-forming metals such as Ta, Al, and Ir can form interfacial layers at intermediate temperatures that block transport with both forward and reverse biases. Higher temperatures degrade these blocking layers. Higher initial bulk native defect densities promote additional reactions and defects that accelerate these effects.

The DRCLS, plasma processing, and metallization techniques have been described previously.<sup>5</sup> We exposed several bulk ZnO single crystals from two vendors to a 20% O<sub>2</sub>-80% He remote plasma for 1 h, then patterned sets of 5–6 each, 30 nm thick, and 0.4 mm diameter contacts of Ta, Al, Ir, Ni, Pt, Pd, and Au on each (0001̄) O-polar surface using filament evaporation without intervening air exposure or electron beam evaporation following air exposure. The ZnO substrates varied in growth technique, deep level defect density, and near band edge (NBE) emission intensity. Depending on the intensity ratio *R* of deep level versus NBE emissions, these crystals are termed “high” (e.g., *R* ≈ 1) or “low” (e.g., *R* ∼ 10<sup>-3</sup>) defect. A JEOL 7800F ultrahigh vacuum scanning electron microscope provided spatially localized excitation through the metal diodes of the ZnO interfaces versus the bare surface next to the diodes. For incident electron beam energies *E<sub>B</sub>* = 2, 5, 10, and 20 keV, Monte Carlo simulations of the electron cascade yield depths of peak electron-hole pair creation *U*<sub>0</sub> ∼ 55, 85, 330, and 990 nm, respectively, below the free ZnO surface. Peak excitation through 30 nm metal overlayers for *E<sub>B</sub>* = 2, 5, 10, and 20 keV corresponds to *U*<sub>0</sub> ∼ -20 (inside the metal), 40, 270, and 960 nm, respectively, varying slightly with metal density. For most metals, a 5 keV beam through the 30-nm-thick metal overlayer and a 2 keV beam into the bare ZnO surface have comparable *U*<sub>0</sub>. Optical transmission through the various metals showed negligible variation across the 1.4–6 eV spectral range. Schottky barriers and ideality factors were extracted from *I-V* curves using thermionic field emission analysis. We measured 10 K DRCL spectra and *I-V* characteristics of patterned surfaces following 1 h annealing at

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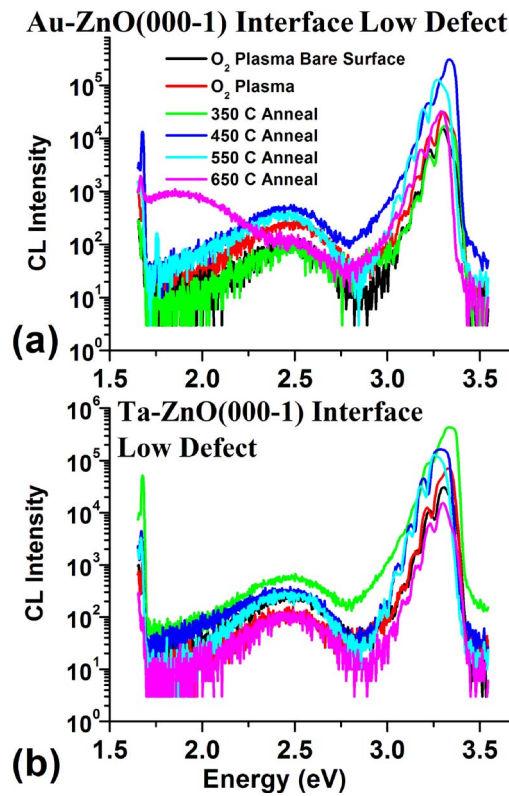


FIG. 1. (Color online) 5 keV DRCLS of 30 nm (a) Au and (b) Ta deposited on low defect (000 $\bar{1}$ ) ZnO. For Au, annealing induces only slight changes for  $T < 650$  °C but a large  $\sim 2$  eV peak at 650 °C. Initial Ta deposition triples 2.5 eV emission, but annealing induces no  $\sim 2$  eV emission or further 2.5 growth.

temperatures up to 650 °C in a tube furnace with 1 atm flowing Ar.

Previously, we showed that metals induce native point defects at ZnO interfaces with CL emissions at 2.1, 2.5, and  $\sim 3$  eV<sup>5</sup> similar to energies reported previously for Zn-rich or poor crystal growth.<sup>6</sup> Among possible native defects, Zn and O vacancies are predicted to be the most energetically favorable;<sup>7</sup> positron annihilation<sup>8</sup> and electron paramagnetic resonance<sup>9,10</sup> spectroscopies associate the 2.1 and 2.5 eV optical transitions with Zn and O vacancies. Elevated temperatures produce large changes in these emissions, depending on the metal and the bulk native defect concentration. Figure 1 presents DRCL spectra for (a) Au and (b) Ta on low defect ZnO(000 $\bar{1}$ ). Annealing up to  $T = 550$  °C leaves the Au/ZnO  $I(2.5 \text{ eV})/I(\text{NBE})$  ratio nearly unchanged and introduces no new spectra features. However, at 650 °C, new emission appears at  $\sim 2$  eV that dominates the deep level spectra. Significantly, Au forms a eutectic with Zn at 625 °C (Ref. 11) and an  $\sim 2.1$  eV emission has been reported with Zn-deficient growth,<sup>6</sup> suggesting Au–Zn alloying that extracts Zn from the substrate. In contrast,  $I(2.5 \text{ eV})/I(\text{NBE})$  increases by more than three times with initial Ta deposition<sup>5</sup> but adds no emission at  $\sim 2$  or 2.5 eV up to 650 °C.

$I$ - $V$  curves display electrical features that correlate with these DRCL spectra and reflect thermal stability up to 550 °C for low defect ZnO. Figure 2(a) shows that Au diodes remain strongly rectifying (barrier  $\Phi_B = 0.46$  eV and ideality factor  $n = 4.30$ ) with increased Schottky barrier  $\Phi_B = 0.54$  eV and lower ideality  $n = 1.47$  following a 450 °C annealing. This is in contrast to thermal instability reported

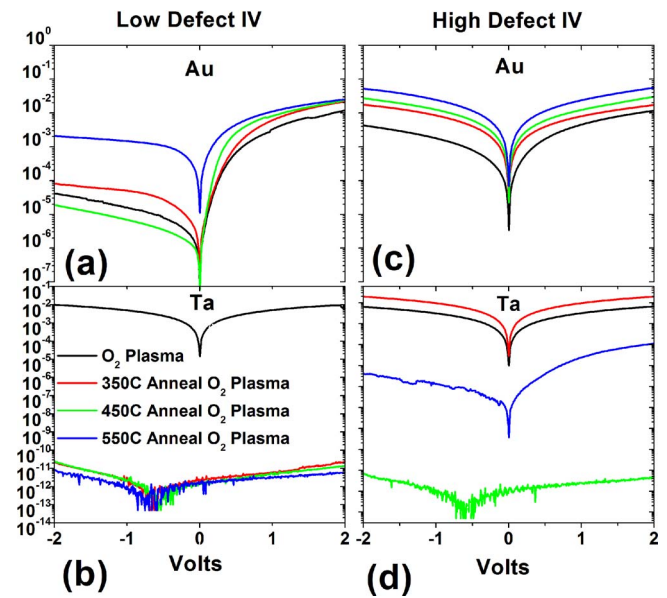


FIG. 2. (Color online) Low defect  $I$ - $V$  characteristics show (a) Au–ZnO Schottky contacts improving at  $T = 450$  °C and remaining rectifying up to a 550 °C annealing and (b) annealed Ta contacts blocking and stable up to 550 °C. High defect  $I$ - $V$  characteristics show (c) Au Schottky barrier steadily degrading starting at 350 °C and (d) Ta contacts that become blocking at 450 °C with leakage increasing at 550 °C. Both metals show lower thermal stability vs low defect ZnO.

elsewhere<sup>12</sup> for Au–ZnO contacts and, significantly, to our high defect ZnO studies. At 650 °C,  $\Phi_B$  degrades to 0.43 eV with  $n = 1.80$ .

Figure 2(b) illustrates the formation of stable, blocking Ta–ZnO contacts. Initially Ohmic, they become blocking following a 350 °C annealing and remain blocking at higher temperatures. Leakage currents are  $< 10^{-11}$  A ( $1.6 \times 10^{-10}$  A/cm<sup>2</sup>). Since Ta oxidation is highly exothermic,<sup>13</sup> this suggests the formation of an insulating oxide layer by extracting O from the substrate. As with Au, the Ta contacts' thermal stability is consistent with the low defect concentrations evident from DRCL spectra and the major effect of such defects on electrical properties.

Figure 3 shows a similar qualitative difference in spectral features between Au and Ta contacts on high defect ZnO. For both metals, the bare ZnO  $R = I(\text{deep level})/I(\text{NBE})$  intensities are  $\geq 1$ . Au deposition increases 2.1 and 3 eV emissions, which increase proportionally with annealing. At 650 °C, 2.1 eV defect emission again dominates. In contrast, both 2.1 and 2.5 eV emissions are evident for Ta diodes, with spectra dominated by 2.5 eV emission for intermediate temperatures, as with Fig. 1(b). However, unlike Fig. 1(b), the balance of 2.1 vs 2.5 eV emissions reverses at 650 °C. These defect changes are reflected in corresponding  $I$ - $V$  spectra shown in Fig. 2(c). Here, Fig. 2(c) displays the initially rectifying characteristics, corresponding to a 0.43 eV barrier ( $n = 3.70$ ). However, this barrier degrades steadily with elevated temperatures starting with 350 °C. Likewise, Fig. 2(d) displays initially Ohmic features that become blocking only at 450 °C. The oxide layer responsible for this blocking is evident from the 5 keV DRCL spectra [inset of Fig. 3(b)], displaying new emission at  $\sim 4.1$  eV [Ta<sub>2</sub>O<sub>5</sub> band gap  $\sim 4.2$  eV (Ref. 14)] that appears only after the 550 °C annealing. Significantly, this blocking feature degrades with 650 °C annealing (leakage current increases by  $\sim 10^5$ ) and this 4.1 eV emission disappears. Coupled with the increased

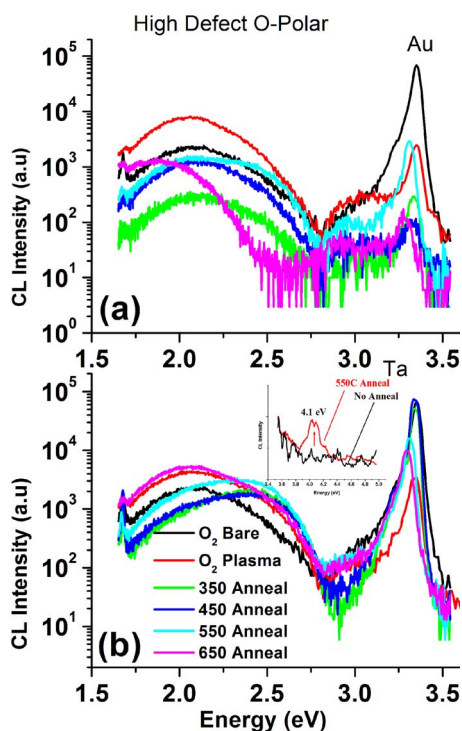


FIG. 3. (Color online) 5 keV DRCLS of 30 nm (a) Au and (b) Ta on high defect (0001) ZnO. Intense 2.1, 2.5, and 3.0 eV emissions are dominated by  $\sim 2.1$  eV emission for Au diodes at 650 °C. For Ta contacts, the 2.5 eV intensity increases with Ta deposition and subsequent annealing up to 550 °C. The inset shows  $\sim 4.1$  eV peak associated with Ta oxide that appears only at 550 °C.

defect emissions in Fig. 3(b), these changes suggest that the oxide layer becomes less insulating as additional near-interface defects form.

For both high and low defect ZnO, Au and Ta contacts produce qualitatively different DRCLS and  $I$ - $V$  features. Similar differences are evident for Pd and Pt which, as with Au, alloy with Zn at elevated temperature, versus Al and Ir, which, as with Ta, form oxides.<sup>15</sup> Thus the increased 2.1 (2.5) eV emissions for Au (Ta) can be associated with Zn (O)-deficient defects near the metal interface. Furthermore, Figs. 2(c), 2(d), and 3 demonstrate that high defect ZnO has lower thermal stability for both Au and Ta contacts. Taken together, these results demonstrate that metals on ZnO form thin interfacial alloy or oxide layers whose nature depends on thermodynamic driving forces. These interfacial layers require either Zn or O atoms from the ZnO, resulting in Zn- or O-deficient layers near the interface only nanometers thick. For Au on low defect ZnO, the Schottky barrier remains stable and alloying begins only at temperatures above the known eutectic, while for high defect material, the Schottky barrier degrades steadily as resident defects redis-

tribute. The Zn-deficient emission dominates only above the eutectic temperature. For Ta on low defect ZnO, a blocking layer associated with O-deficient defects forms at low temperatures and remains stable with increasing temperature, while for high defect ZnO, the contact is Ohmic up to intermediate temperatures and its 550 °C blocking layer becomes leaky at higher temperatures. This contrast between low and high defect ZnO contacts and their defect emission demonstrates that the presence of high defect concentrations promotes interface alloying and reactions that produce additional defects that, in turn, degrade Schottky barriers and blocking layers. In order to achieve high Schottky barriers or blocking layers, defects at the intimate metal-ZnO interface must be minimized. For alloying metals such as Au, subeutectic temperatures are required to preserve Schottky barriers. For oxidizing metals such as Ta, temperatures must be high enough to promote oxide thicknesses sufficient to block current without concomitant defect concentrations high enough to disrupt this layer.

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